



PROCOPY RESOLUTION TEST CHART

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FINAL REPORT



ELECTROCHEMICAL AND OPTICAL ELECTRON TRANSFER PROCESSES

Paul Delahay Principal Investigator

Period: April 1, 1982 to September 30, 1986

New York University Department of Chemistry New York, NY

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Inner-sphere reorganization (19. ABSTRACT (Continue on reverse if necessary and identify by block number)										
A summary of significant result £1) Nonequilibrium electronic pobservation of this effect and detailed theory accounting for in optical electron transfer: between optical electron transfer theoretical solvation model of mental verification of this modin aqueous solution; £(d) applic £(3) Ionization energies of liquitive curves. A list of reports	ts is given cove polarization and subsequent deta experimental read a) treatment of fer and thermal (inner-sphere redel; {c) application to the gastids from energy	ring the thre loss in opti iled experime sults. (2) I f cations and electron exchorganization tion to the es-liquid shif distribution	ical electro ental study; inner-sphere i metal comp nange; {b) d for univale energetics o ft for photo	on tra (ansfer: develop lear red s and co opment o nions an ion/radi tron emi	(a) first pment of a organization or the dexperision.				
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SUMMARY OF SIGNIFICANT RESULTS

Three broad areas were covered:

- (1) Nonequilibrium electronic polarization and loss in optical electron transfer
 - (a) First observation of this effect and subsequent detailed experimental study (report 3)
 - (b) Development of a detailed theory accounting for experimental results (reports 3, 6, 8 and 11)

Yield spectra for photoelectron emission by liquids and solutions exhibit a fine structure which is essentially determined by the nature of the solvent and not by the species being photoionized. This fine structure was shown to arise from nonequilibrium electronic processes (polarization, loss) arising from dielectric dispersion of the solvent. Theoretical and experimental fine structure features agree extremely well. This effect, which was first observed in our laboratory, is the electronic counterpart of nuclear reorganization (Marcus, Sutin, etc.)

- (2) Inner-sphere nuclear reorganization in optical electron transfer
 - (a) Treatment of cations and metal complexes and correlation between optical electron transfer and thermal electron exchange (report 4)
 - (b) Development of the theoretical solvation model of inner-sphere reorganization for univalent anions and experimental verification of this model (reports 4 and 9)
 - (c) Application to the energetics of anion/radical couples in aqueous solution (report 10)
 - (d) Application to the gas-liquid shift for photoelectron emission (report 5)

Energies of inner-sphere reorganization were derived from a bond stretching model for optical electron transfer involving <u>cations</u> and metal complexes. This made it possible to correlate thermal and <u>optical</u> electron transfer processes. Results are in agreement with experiment. The energy of inner-sphere reorganization of univalent <u>anions</u> was calculated from a <u>solvation</u> model based on a multipole expansion accounting for ion-solvent electrostatic interactions. Other contributions (London dispersion, Born repulsion, etc.) were also taken into account. Agreement with experiment is achieved.

(3) Ionization energies of liquids from energy distribution, quantum yield and second derivative curves

These three methods of determining ionization energies were investigated and compared for eight liquids (report 7).

TECHNICAL REPORTS AND PUBLICATIONS

- 1. P. Delahay, "Anomalous reorganization free energies in optical electron transfer in solution," Technical Report No. 1 (June 1982); Chem. Phys. Lett. 90, 425 (1982).
- 2. P. Delahay, "Dielect ic dispersion in optical electron transfer in solution," Technical Report No. 2 (March 1983); Chem. Phys. Lett. 96, 613 (1983).
- 3. P. Delahay and A. Dziedzic, "Dispersion spectroscopy of optical electron transfer in solution," Technical Report No. 3 (February 1984); J. Chem. Phys. 80, 5381 (1984).
- 4. P. Delahay and A. Dziedzic, "Inner-sphere reorganization in optical electron transfer," Technical Report No. 4 (March 1984); J. Chem. Phys. 80, 5793 (1984).
- 5. P. Delahay and A. Dziedzic, "Gas-liquid correlation of ionization energies," Technical Report No. 5 (April 1984); Chem. Phys. Lett. <u>108</u>, 169 (1984).
- 6. P. Delahay and A. Dziedzic, "Solvation and dielectric dispersion in optical electron transfer," Technical Report No. 6 (July 1984); J. Chem. Phys. 81, 3678 (1984).
- 7. K. P. Cheung, I. Watanabe, A. Dziedzic, K. von Burg and P. Delahay, "Ionization energies of liquids from energy distribution, quantum yield and second derivative curves," Technical Report No. 7 (March 1985); J. Electron Spectrosc. 36, 245 (1985).
- 8. P. Delahay and A. Dziedzic, "Nonequilibrium electronic polarization of the solvent in photoionization," Technical Report No. 8 (July 1985); J. Chem. Phys. $\underline{84}$, 936 (1986).
- 9. P. Delahay and A. Dziedzic, "Discrete model for inner-sphere reorganization of anions," Technical Report No. 9 (May 1986); Chem. Phys. Lett., 128, 378 (1986).
- 10. P. Delahay and A. Dziedzic, "Nuclear reorganization in the photoionization of anions in solution," Technical Report No. 10 (July 1986); Proc. Indian Acad. Sci. (Chem. Sci.), in press (by invitation from the editor; issue in honor of K. S. G. Doss).
- 11. P. Delahay and A. Dziedzic, "Transition dipole-solvent interaction in photoionization," Technical Report No. 11 (September 1986); Chem. Phys. Lett., in press.
- 12. P. Delahay and A. Dziedzic, "Transition dipole-solvent interaction in photoionization in solution," Technical Report No. 12 (September 1986); J. Electroanal. Chem., in press (by invitation from the editor; special issue

- in honor of H. Gerischer on his retirement as Director of the Fritz-Haber-Institut, Berlin).
- 13. In addition to the above reports and publications, the principal investigator wrote Chapter 2 on photoelectron emission spectroscopy of liquids and solutions in "Electron Spectroscopy," vol. 5, C. R. Bundle and A. D. Baker, editors (Academic Press, London, 1984), pp. 123-196.

PERSONNEL

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Andrew Dziedzic, graduate student, Ph.D. degree, and postdoctoral fellow (now with Goldman Sachs)



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